

**EUROPEAN PATENT APPLICATION**

Application number: 88201914.4

Int. Cl. 4: **C08G 63/62 , C08K 3/22 ,  
C08L 69/00**

Date of filing: 06.09.88

Priority: 04.11.87 NL 8702632

Date of publication of application:  
10.05.89 Bulletin 89/19

Designated Contracting States:  
DE FR GB IT NL

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Impact modified P-Cumyl-end capped PC.

The invention relates to an aromatic polycarbonate having 4-cumylphenyl terminal groups and a low relative viscosity of less than 1.24. The invention also relates to polymer mixtures which comprise the aromatic polycarbonate just mentioned and one or more agents to improve the impact strength.

**EP 0 315 226 A1**

**Polycarbonate having a low relative viscosity and polymer mixtures.**

The invention relates to an aromatic polycarbonate having terminal 4-cumylphenyl groups.

Aromatic polycarbonate is a known polymer. Chain stoppers for controlling the molecular weight of the polymer are sometimes used in the preparation of aromatic polycarbonate.

5 Phenol is the most generally used chain stopper. The use of 4-cumylphenol as a chain stopper is known from JP-A-57(1982)-133149. The use of chain stoppers leads to the incorporation in the polymer of terminal groups derived from the chain stopper (namely 4-cumylphenyl groups).

It is generally known that the flow properties of polymers can be improved by reducing the molecular weight of the polymer. Limits are imposed upon such reduction: the mechanical properties of the polymer decrease when the molecular weight is reduced too far. This also applies to aromatic polycarbonate. 10 Aromatic polycarbonate having a low molecular weight (corresponding to a relative viscosity of less than 1.24) has a much lower notch impact value at room temperature than normal polycarbonate having a relative viscosity of, for example, 1.29.

The invention is based on the discovery that aromatic polycarbonate having terminal 4-cumylphenyl groups also has good mechanical properties, for example, a good notch impact value, also with a low molecular weight, in particular also at reduced temperatures.

In general, the impact strength of a polycarbonate decrease considerably when the polycarbonate is mixed with an inorganic filler/pigment. The polycarbonate according to the invention has the surprising property that it maintains its impact strength after mixing with titanium dioxide.

20 The aromatic polycarbonate according to the invention is characterised in that it has a relative viscosity of less than 1.24. The relative viscosity is preferably between 1.19 and 1.24.

The polycarbonate powder according to JP-A-57(1982)-133419 has a molecular weight of 24,700 to 25,600, which corresponds to a relative viscosity of approximately 1.25-1.28.

The invention also relates to an aromatic polycarbonate as defined in Claim 1, which is mixed with 0- 25 10% by weight of titanium dioxide.

The aromatic polycarbonate according to the invention may also be used in polymer mixtures. The invention also relates to such mixtures.

The polymer mixtures which comprise the aromatic polycarbonate according to the invention and one or more agents to improve the impact strength are of particular importance.

30 It has been found that the addition of a comparatively small quantity of 0.1-4% by weight of one or more agents to improve the impact strength results in polymer mixtures which combine a good flow with a good impact strength at low temperatures. Larger quantities of the agent to improve the impact strength result in a deterioration of the flow.

A mixture of two different agents to improve the impact strength is preferably used in the polymer mixture according to the invention, namely a mixture of:

B1. a core-shell graft copolymer built up from a rubber-like core, built up substantially from an acrylate rubber or a butadiene rubber and one or more shells grafted thereon of a rigid polymer built up substantially from an alkylacrylate and/or alkylmethacrylate and/or vinylaromatic compound, for example, styrene and/or acrylonitrile and

40 B2. a block copolymer built up from rubber-like siloxane blocks and polycarbonate blocks.

In addition to the agents to improve the impact strength mentioned hereinbefore, the polymer mixture according to the invention may comprise one or more of the following constituents: one or more agents to improve the flame-retarding properties, one or more stabilisers, one or more agents to reduce the drip properties in flame tests, one or more pigments, one or more dyes, one or more fillers, one or more 45 reinforcing fibres, for example, glass fibres, lubricants, mould-release agents, plasticisers.

The aromatic polycarbonate according to the invention may also be mixed itself with the constituents mentioned hereinbefore without using agents to improve the impact strength.

The polymer mixture according to the invention may also comprise in particular pigments, for example, titanium dioxide, for example, in a quantity of 0.1-10 parts by weight per 100 parts by weight of the aromatic polycarbonate according to the invention plus the agent or the agents to improve the impact strength. It has been found that the addition of titanium dioxide only results in a very small reduction of the notch impact value.

The polymer mixture according to the invention may moreover comprise further polymers, for example, polyalkylene terephthalates, for example, polybutylene terephthalate. It is to be preferred, when polyalkylene terephthalates are used, to use 1-100 parts by weight of the polyalkylene terephthalate per 100 parts

by weight of the aromatic polycarbonate according to the invention plus the agent or the agents to improve the impact strength.

Finally, the invention also relates to articles formed from the aromatic polycarbonate according to the invention or from the polymer mixture according to the invention.

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#### The aromatic polycarbonate according to the invention

Aromatic polycarbonates are polymers known per se. They are conventionally prepared according to a so-called interfacial polymerisation process. In this process, phosgene is passed through an aqueous alkaline solution of a dihydric phenol in the presence of an inert organic solvent. A chain stopper is usually added during or shortly before the end of the reaction. 4-Cumylphenol is always used as a chain stopper in the preparation of the aromatic polycarbonate according to the invention. It is possible to control the molecular weight of the polycarbonate by dosing the quantity of chain stopper and by the choice of the instant at which the chain stopper is added to the reaction mixture. For the preparation of the polymer according to the invention, all this is controlled so that a polycarbonate having a relative viscosity of less than 1.23 is obtained. Relative viscosity is always to be understood to mean herein the relative viscosity determined according to DIN-standard 7744, vol. 2, in a concentration of 0.5 g of polymer dissolved in 100 ml of dichloroethane at 25° C. The measurements were always carried out using a Ubelohde viscosimeter with a so-called Oc capillary.

It is also possible to obtain a polycarbonate according to the invention by mixing two or more different polycarbonates. For example, by mixing, in approximately equal quantities by weight, a polycarbonate having a relative viscosity of 1.24 with a polycarbonate having a relative viscosity of 1.20. Both polycarbonates must have terminal 4-cumylphenyl groups.

As indicated above, the polymer mixture according to the invention comprises the aromatic polycarbonate according to the invention and one or more agents to improve the impact strength.

The addition of one or more agents to improve the impact strength to the polycarbonate according to the invention results in a polymer mixture which has a good flow and a good impact strength at low temperatures. For this purpose, only comparatively small quantities of the agent or the agents to improve the impact strength need be added.

In order to obtain the same good impact strength at low temperatures for polymer mixtures based on a polycarbonate having the same low relative viscosity but with terminal phenyl groups, it is necessary to add larger quantities of the agent to improve the impact strength. However, this usually results in a deterioration of the flow properties.

A mixture of two agents to improve the impact strength is preferably used in the polymer mixtures according to the invention, namely a mixture of:

B1. a core-shell graft copolymer built up from a rubber-like core, built up substantially from an acrylate rubber or a butadiene rubber and one or more shells grafted thereon of a rigid polymer built up substantially from an alkylacrylate and/or alkylmethacrylate and/or vinylaromatic compound, for example, styrene and/or acrylonitrile, and

B2. a block copolymer built up from rubber-like silicon blocks and polycarbonate blocks.

Core-shell graft copolymers as meant hereinbefore are generally known. For this purpose, reference may be made, for example, to US-A-3,426,101; US-A-3,655,826; US-A-4,096,202; US-A-4,180,494.

Block copolymers built up from rubber-like silicon blocks and polycarbonate blocks are also known.

For this purpose, reference may be made, for example, to US-A-2,999,845; US-A-3,189,662; US-A-3,419,634; US-A-3,679,774 and EP-A-0193757.

The polymer mixture according to the invention may be prepared according to any conventional method of preparing polymer mixtures. The polymer mixture according to the invention is preferably prepared by compounding in an extruder.

The invention will now be described in greater detail with reference to the ensuing specific examples.

#### Example 1

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The preparation of an aromatic polycarbonate

Various aromatic polycarbonates were prepared by means of interfacial polymerisation starting from

bisphenol A and phosgene. A chain stopper was always used in the preparation: 4-cumylphenol was used in the preparation of polymers A and B, and phenol was used in the preparation of polymers C and D. The chain stopper was used in a concentration of 6.2 mol% for polymer A, 4.7 mol% for polymer B, 6.2 mol% for polymer C, and 4.6 mol% for polymer D.

In this manner four polymers were obtained having a relative viscosity as indicated in Table A.

The notch impact value according to Izod was measured at different temperatures. The results are also recorded in Table A.

The melt flow index (MFI) was also determined according to DIN 53735 or ISO 1133 at 300 ° C under a load of 12 N for 10 minutes.

Table A

Polymer	A	B	C	D
Terminal group	4-cumylphenyl	4-cumylphenyl	phenyl	phenyl
relative viscosity	1.20	1.23	1.20	1.25
MFI (g/10 min)	55	25	50	20
Izod notch impact value (J/m)				
Room temp.	300	620	110	620
0 ° C	100	510	100	120
-10 ° C	100	250	100	100
-20 ° C	100	170	100	170

### Example II

Polymer B was compounded in an extruder with various quantities of barium sulphate. The same was done with polymer D. In this manner various compositions were obtained. Test rods for measuring the Izod notch impact value were injection-moulded from these compositions. The notch impact values of these rods were determined. The various compositions and the associated notch impact values are recorded in Table B.

Table B

IZOD Notch impact value  
(J/m; room temperature)

#### Polymer B

+ 0% by weight of BaSO <sub>4</sub>	656
+ 1% by weight of BaSO <sub>4</sub>	170
+ 3% by weight of BaSO <sub>4</sub>	158

Table B (ctd.)

Polymer D	625
+ 0% by weight of BaSO <sub>4</sub>	
+ 1% by weight of BaSO <sub>4</sub>	245
+ 3% by weight of BaSO <sub>4</sub>	135

It may be seen from Table B that the polymer according to the invention (polymer B), as well as the known polymer (polymer D), after mixing with barium sulphate have a bad notch impact value.

The polymers B and D mentioned hereinbefore were then compounded with various quantities of titanium dioxide. The notch impact value was determined again. The results are recorded in Table C.

Table C

IZOD Notch impact value  
(J/m; room temperature)

Polymer B	
+ 0% by weight of TiO <sub>2</sub>	656
+ 1% by weight of TiO <sub>2</sub>	643
+ 2% by weight of TiO <sub>2</sub>	634
+ 5% by weight of TiO <sub>2</sub>	636
Polymer D	
+ 0% by weight of TiO <sub>2</sub>	625
+ 1% by weight of TiO <sub>2</sub>	541
+ 2% by weight of TiO <sub>2</sub>	164

It may be seen from Table C that the polymer according to the invention (polymer B) is sensitive to mixing with titanium dioxide only to a very slight extent. The known polymer D on the contrary shows a very strong sensitivity to titanium dioxide.

### Example III

Various polymer mixtures were prepared using on the one hand a mixture of equal parts by weight of polymer A and polymer B, and on the other hand Polymer C and Polymer D (according to example I). Each of the mixtures thus obtained was compounded in an extruder with two different agents to improve the impact strength and with a mixture of these two agents to form a polymer mixture. The following constituents were used as an agent to improve the impact strength:

Paraloid®KM 653:	a core-shell copolymer commercially available from Rohm & Haas having a core based on a butadiene rubber and a shell substantially built up from methyl methacrylate.
LR 3320 :	a polycarbonate-polysiloxane block copolymer commercially available from General Electric Company having blocks with approximately 9 siloxane units.

The notch impact value according to IZOD at different temperatures, the "fixed plate impact"

according to DIN 53443 at  $-30^{\circ}\text{C}$  and the melt flow index were determined for the resulting polymer mixtures. The transition temperature between ductile and brittle fracture was also determined (D/B).

The results are recorded in Table D hereinafter for the polymer mixtures based on a polymer according to the invention (with terminal 4-cumylphenyl groups). The results for polymer mixtures based on a polymer having the same intrinsic viscosity but a terminal group (phenyl group) which is not in accordance with the invention are recorded in Table E.

Table D

Composition No. (parts by weight)	1	2	3	4	5	6	7
Polycarbonate A	50	50	50	50	50	50	50
Polycarbonate B	50	50	50	50	50	50	50
LR 3320	-	0.5	1.5	-	-	0.5	1.5
KM 653	-	-	-	0.5	1.5	1.0	1.0
Properties							
Izod notch impact value (J/m)							
Room temperature	621	621	619	639	601	615	599
$10^{\circ}\text{C}$	502	591	585	585	562	584	563
$0^{\circ}\text{C}$	462	261	306	313	460	473	533
$-5^{\circ}\text{C}$	156	216	215	465	526	475	520
$-10^{\circ}\text{C}$	159	146	175	143	294	199	461
$-15^{\circ}\text{C}$	-	-	-	-	204	177	349
$-20^{\circ}\text{C}$	-	-	-	-	-	-	223
Flexed Plate impact (J)							
$-30^{\circ}\text{C}$	102	97	91	119	108	117	123
MFI (g/10 min.)	39	38	37	37	39	38	39
Ductile/Brittle Transition temp. in IZOD impact test ( $^{\circ}\text{C}$ )	-2	5	-2	-7	-7	-7	-17

Table E

Composition No. (parts by weight)	8	9	10	11	12	13	14
Polycarbonate C	50	50	50	50	50	50	50
Polycarbonate D	50	50	50	50	50	50	50
LR 3320	-	0.5	1.5	-	-	0.5	1.5
KM 653	-	-	-	0.5	1.5	1.0	1.0
Properties							
Izod notch impact value (J/m)							
Room temperature	103	347	570	212	620	590	610
$10^{\circ}\text{C}$	97	222	179	117	340	487	566
$0^{\circ}\text{C}$	103	120	137	105	159	181	210
Flexed Plate impact (J)							
$-30^{\circ}\text{C}$	91	109	113	86	88	106	103
MFI (g/10 min.)	37	38	36	39	38	38	38
Ductile/Brittle Transition temp. in IZOD impact test ( $^{\circ}\text{C}$ )	>RT	RT	15	>RT	10	5	5

<sup>\*)</sup> RT = room temperature.

Comparison of the results recorded in Tables D and E demonstrate that the polycarbonate according to the invention and polymer mixtures based on that polycarbonate have a better combination of low temperature impact strength and flow than the known polycarbonate. The D/B temperatures with such a flow

are approximately 15° C lower. When the polymer mixtures according to Table E are to be given an equal low temperature impact strength, a larger quantity of LR 3320 and/or KM 653 would have to be added; this would lead to a considerable increase of the viscosity of the melt and an unacceptable increase of the melt flow index.

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## Claims

1. An aromatic polycarbonate having terminal 4-cumylphenyl groups, characterised in that the aromatic polycarbonate has a relative viscosity of less than 1.24.

2. An aromatic polycarbonate as claimed in Claim 1, characterised in that it has been mixed with 0.1-10% by weight of titanium dioxide.

3. A polymer mixture which comprises an aromatic polycarbonate and one or more agents to improve the impact strength, characterised in that the polymer mixture comprises the following constituents:

15 A. an aromatic polycarbonate having a relative viscosity of less than 1.24 comprising terminal groups derived from 4-cumylphenol as the aromatic polycarbonate.

B. one or more agents to improve the impact strength, in which the quantity of constituent A is between 96 and 99.9% by weight and the quantity by weight of constituent B is between 0.1 and 4% by weight calculated with respect to the sum of constituents A and B.

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4. A polymer mixture as claimed in Claim 3, characterised in that constituent B consists of a mixture of two agents to improve the impact strength, namely:

B1. a core-shell graft copolymer built up from a rubber-like core substantially built up from an acrylate rubber or a butadiene rubber and one or more shells of a rigid polymer grafted thereon and built up substantially from an alkyl acrylate and/or alkylmethacrylate and/or vinylaromatic compound, and

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B2. a block copolymer built up from rubber-like siloxane blocks and polycarbonate blocks.

5. A polymer mixture as claimed in Claim 3, characterised in that the polymer mixture comprises, in addition to the constituents mentioned sub A and B, one or more of the following constituents: one or more agents to improve the flame-retarding properties, one or more stabilisers, one or more agents to reduce the drip properties in flame tests, one or more pigments, one or more dyes, one or more fillers, one or more reinforcing fibres, for example, glass fibres, lubricants, mould release agents, plasticisers.

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6. A polymer mixture as claimed in Claim 5, characterised in that the polymer mixture comprises as a pigment 0.1-10 parts by weight of titanium dioxide per 100 parts by weight of A + B.

35 7. A polymer mixture as claimed in Claim 3, characterised in that the polymer mixture comprises 1-100 parts by weight of a polyalkylene terephthalate per 100 parts by weight of A + B.

8. Articles formed from the aromatic polycarbonate as claimed in Claim 1 or 2 or from the polymer mixture as claimed in any of the Claims 2-7.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	CHEMICAL ABSTRACTS, vol. 84, no. 22, 1976, page 50, no. 151634v, Columbus, Ohio, US; & JP-A-76 20 993 (MITSUBISHI GAS CHEMICAL CO., INC.) 19-02-1976 * Abstract *	1,2	C 08 G 63/62 C 08 K 3/22 C 08 L 69/00
Y	EP-A-0 010 602 (BAYER) * Claims 1-3 *	1,2	
D,A	PATENT ABSTRACTS OF JAPAN, vol. 6, no. 231 (C-135)[1109], 17th November 1982; & JP-A-57 133 149 (IDEMITSU KOSAN K.K.) 17-08-1982 * Abstract *	1	
A	EP-A-0 239 157 (GENERAL ELECTRIC) * Claims 1-8 *	1,3,7,8	
A	EP-A-0 164 477 (GENERAL ELECTRIC) * Claims 1-4,8 *	1,3,4,5	
A	WO-A-8 000 708 (GENERAL ELECTRIC) * Claims 1,2 *	1,2,6	TECHNICAL FIELDS SEARCHED (Int. Cl.4)  C 08 G C 08 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12-01-1989	Examiner DECOCKER L.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document			